

CATION ADSORPTION IN A
SANDY FOREST SOIL IN
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Abstract

The adsorption of NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} , as controlled by ion exchange, was investigated in an acid pine forest soil. The objective was to describe changes of the adsorbed amounts as functions of the concentrations in the solution for use in transport models. These changes were registered when soil samples were equilibrated with dilute salt solutions. The situation of low concentrations in the natural soil as well as fertilization with NH_4^+ was simulated in the experiments.

The adsorption of monovalent ions could be expressed entirely as the function of ionic ratios in the solution, while the level of concentration had to be considered for divalent ions. Changes in the sum of adsorbed ions in the experiments indicated that some additional ion species besides those analysed were involved. The buffer powers for different ions were calculated and their influence on uptake and leaching described. It was concluded that adsorption is unimportant for these processes when there is a steady input, while adsorption has an influence in situations of variable input.

Introduction

The ecological significance of cation adsorption in soil lies in the effect on leaching, uptake by roots, and other soil processes that can be limited by transport rates in the pore system. Transport models require relationships between concentrations in the solution and quantities in the solid phase (Ulrich et al 1979). Such quantity/intensity relationships are difficult to describe for acid soils, where exchange between a large number of ion species must be considered simultaneously. Empirical descriptions of the relations have to be simplifications of the real system, valid only under specified conditions. The objectives of the investigations must be clearly defined in order to make these simplifications. In this case, the objectives have been to describe the ion exchange controlling the adsorption of NH_4 , Na, K, Ca and Mg at concentration levels occurring in a natural pine forest soil, and at increased NH_4 levels, such as may be caused by fertilization. The relationships, the so-called adsorption isotherms, have been formulated for inclusion in transport models.

Methods

Investigation site and sampling

The investigated soil is a sandy iron-podsol in an old Scots pine forest in Central Sweden (Swedish Coniferous Forest Project, site Ih5). Some general characteristics of this soil are listed in Table 1. The litter layer on the soil surface was not included in the investigation. The cation exchange capacity is very low and the content of fine material small, making soil organic matter important for the exchange capacity. Aluminium dominates the exchange complex. The estimates of exchangeable Al were larger in the upper mineral soil layer than in the lower one. Apart from a real difference of Al-levels in the soil, the pH appearing in the NH_4Cl -extracts can be expected to have had an influence on the determinations.

Soil samples for adsorption experiments were collected from three or four soil profiles in the forest stand. The sampling was repeated whenever material was needed, so different experiments have been conducted on different samples.

The suitability of the few samples for quantitative estimates relevant for the stand can be questioned, but qualitative conclusions are valid. Material was taken from the humus layer and from 0-10cm and 10-20 cm in the mineral soil. Coarse roots were removed from the material prior to its use in the experiments. No sieving was performed as it was considered too destructive.

Experimental method

Small portions of the soil samples were equilibrated with salt solutions having total concentrations of the investigated cations from 300 to 2000 $\mu\text{eq}\cdot\text{l}^{-1}$ and in some "fertilization" experiments (see below) up to 10 000 $\mu\text{eq}\cdot\text{l}^{-1}$. The ionic ratios of the solutions were varied to bring about ion exchange in concentration ranges not too different from those of the soil solution. The salt solutions were mixtures of the chlorides of NH_4 , Na, K, Ca and Mg. Ten g of fresh humus layer material or 30 g of fresh mineral soil was shaken with 100 ml of solution for two hours, or in some cases for half an hour. After filtration NH_4 , Na, K, Ca and Mg were determined in the filtrates as well as in the original salt solution. The methods of chemical analysis were flame emission for Na and K, atomic absorption for Ca and Mg (interferences counteracted with La-additions) and gas-selective electrode for NH_4 .

Adsorption or desorption (ΔG , $\mu\text{mole}\cdot\text{g}^{-1}$) that occurred during the equilibrations was determined from the concentration differences between the original salt solutions and the equilibrium solutions, calculated on a dry weight basis. The differences were regarded as a change from a reference state described by the exchangeable amounts in Table 1. The reference levels of NH_4 were determined by extraction with 1% KAlSO_4 at each experiment. The concentrations of all the ions were measured in the solution after the equilibration to yield the intensity variable.

Definitions

Before the experiments are described in further detail, some denotations and variables have to be defined. C_A is the solution concentration (μM) of the ion under consideration, indicated by C_{NH_4} , C_{Na} , C_{K} , C_{Ca} and C_{Mg} for the

different ions. The equivalent sum of these concentrations is called C_T ($\mu\text{eq}\cdot\text{l}^{-1}$). The remaining concentration when C_A is subtracted from C_T is denoted C_R ($\mu\text{eq}\cdot\text{l}^{-1}$). Monovalent and divalent ions constituting C_R have the concentrations C_I and C_{II} respectively (μM). Intensity variables (I) of the solution are defined as $\log(C_A^2 C_I^{-1} C_{II}^{-0.5})$ for the monovalent ions and $\log(C_A C_I^{-1} C_{II}^{-0.5})$ for the divalent. Motivations for these formulations are given later. The adsorbed quantities are called G ($\mu\text{mole g}^{-1}$) and can be given the same indices as the concentrations. The sum of adsorbed ions is, for instance, called G_T .

Specific experiments

Two main type of experiments were conducted. In the first type (type 1) the intensity for a certain variable ion was successively changed in a series of equilibrations with soil material by increasing C_A from zero to the level of C_T and simultaneously decreasing C_R in such a way that C_T was kept within a narrow range. The changes of adsorbed amounts (ΔG) were recorded for the ion forming C_A and regressions between I and ΔG were calculated. Na, K, Ca and Mg, except the one forming C_A , were included in C_R at concentrations that were roughly alike for the different ions. Some experiments were repeated with a five-fold increase of the Na portion of C_R and some with NH_4 included in C_R . The regressions obtained between ΔG and I were not significantly affected by the latter variations.

The experiments were repeated at different levels of C_T (Table 2). A larger range of I values was covered at higher C_T levels (Fig 1) as the solution had a greater capacity to influence the equilibrium in these cases. In most type 1 experiments, denoted type 1.1 (Table 2), the resulting levels of C_T after equilibrations had standard deviations that were less than 5% of the means. In a few cases, denoted 1.2, C_T was not successfully kept constant due to errors in the experimental design.

In the second type of experiments (type 2) large additions of NH_4 or NH_4+K were made. These "fertilization" experiments were performed in order to validate the adsorption isotherms obtained in type 1 experiments. Moreover they were included in the calculation of NH_4 isotherms.

During the successive increase of NH_4 or NH_4+K in equilibration series C_R was kept at a steady level. The sizes of the NH_4 and NH_4+K concentrations were in the range from zero to 4000 μM for the mineral soil and up to 10 000 μM for the humus layer. C_T was allowed to increase in these series. Adsorption and desorption of the different ions were recorded.

Different versions of type 2 experiments were performed. On samples from 0-10 cm in the mineral soil they were:

Type 2.1 "Fertilizer" ion NH_4 . Level of C_R about 400 $\mu\text{eq l}^{-1}$.
Na/K ratio 4.

Type 2.2 "Fertilizer" ion NH_4 . Level of C_R about 400 $\mu\text{eq l}^{-1}$.
Na/K ratio 0.4.

Type 2.3 "Fertilizer" ion NH_4 . Level of C_R about 950 $\mu\text{eq l}^{-1}$.
Na/K ratio 4.

Type 2.4 "Fertilizer" ions NH_4+K . Level of C_R about 350 $\mu\text{eq l}^{-1}$.

Types 2.2 and 2.4 were also conducted with humus layer material, with C_R about 200 $\mu\text{eq l}^{-1}$.

Statistical treatment

Linear regressions were calculated according to Snedecor & Cochran (1973). The 95% confidence limits on the prediction of the y-variable were calculated with $t_{0.05} s_y$, s_y being the standard deviation of this prediction. The deviations from 1 of the slopes of some regressions were tested with the t-distributed variable $(p-1)/s_p$, p being the estimate of the slope and s_p its standard deviation.

Results and discussion

Inconstancy of the exchange capacity

Ion exchange should involve equal amounts of adsorbed and desorbed ions. However, a changing adsorbed amount of the recorded ions (G_T) was a characteristic result of the adsorption experiments. The experiments in which C_T was held constant at different levels (type 1.1) revealed that G_T rose as C_T increased. For potassium experiments in the mineral soil layer 0-10 cm, the

average ΔG_T were -0.34 , -0.05 and $0.57 \mu\text{eq g}^{-1}$ at C_T 270, 830 and 1900 $\mu\text{eq l}^{-1}$, respectively. Similar trends were found in all other experiments. The conclusion is that the exchange capacity for NH_4 , Na, K, Ca and Mg increases when the solution is stronger. Increased Na intensities counteracted the effect of rising C_T , but otherwise the ionic composition seemed to be of little importance in this connection. An important question with respect to the adsorption isotherms is, whether the effect of C_T has to be included in the expressions.

The changing G_T indicates the participation of other ions in the exchange processes; Al and H are highly probable in acid soils. The performance of Al and H ions in exchange processes is difficult to reproduce experimentally. A whole range of possible Al species exist, depending on pH, silicates and anions in the solution. The exchange with Al proceeds at a much slower rate than exchange between the base cations (Sivasubramanian & Talibudeen 1972). The reaching of equilibrium may require days even at low water/soil ratios. In these circumstances it is desirable to avoid explicit inclusions of Al and H in the adsorption experiments for other ions.

The large affinity of Al and H to the exchange sites and the large store of Al (Table 1) motivates that these ions can be regarded as independent of the others. The influence from Al and H is unidirectional in that they create the capacity for the exchange between other metal ions. Such a stepwise approach was used for H^+ in peat by André & Pijarowsky (1977). Of course, variations in pH and Al activities would have profound effects on the adsorption of the base cations. In this investigation, Al and pH are treated as an invariable background to the other exchange processes.

Formulations of the adsorption isotherms

Adsorption isotherms that are suitable for transport models should predict adsorption/desorption from the concentrations in the solution. The solution is affected by ion and water transfers occurring in the soil, while the adsorbed amounts have a buffering effect on the concentrations. In acid soils a multiple ion exchange must be considered. A useful intensity parameter (I) is the relative chemical potential (Khanna & Ulrich 1973). In this paper it is given the following form, exemplified for a monovalent ion:

$$\mu = RT \left[2 \ln (C_A 10^{-6}) - \ln (C_I 10^{-6}) - 0.5 \ln (C_{II} 10^{-6}) \right]$$

in which concentrations are used as estimates of activities. The expression is transformed for practical use as follows:

$$I = \log \left(\frac{C_A^2}{C_I \sqrt{C_{II}}} \right) \quad (\mu M^{0.5}) \quad (1)$$

The corresponding variable for divalent ions is

$$I = \log \left(\frac{C_A}{C_I \sqrt{C_{II}}} \right) \quad (\mu M^{-0.5}) \quad (2)$$

The transformations involve multiplications by the factor $(RT \ln 10)^{-1}$ and additions of a term for the change to micromolar concentrations.

The formulations take into account the valency effect, i. e., that only half as many divalent ions compared to monovalent are needed for a given electric potential.

In limited ranges of the intensity variable (I), it can be related to changes of the adsorbed amounts (ΔG) by linear or second degree regressions (Khanna & Ulrich 1973). In this investigation linear regressions between I and ΔG were not applicable for the monovalent ions, although they worked well for the divalent ones. Instead, the following quantity variable was used for both categories of ions:

$$\log G = \log (G_{ex} + \Delta G)$$

where G_{ex} is the extractable amount in Table 1, or, in the case of NH_4 , as determined in connection with the relevant experiments. The resulting regression is

$$\log G = p \cdot I + q \quad (3)$$

where p and q are slope and intercept. This expression can be derived from a formulation of the isotherm having the form

$$\frac{G^2}{G_I \sqrt{G_{II}}} = \left(\frac{C_A^2}{C_I \sqrt{C_{II}}} \right)^{2p} \quad (4)$$

for monovalent ions. G_I and G_{II} are treated as a background included in the intercept, as ΔG_I and ΔG_{II} corresponding to a certain ΔG_A are rather small in relation to the size of their stores. This simplification is one factor that might limit the validity of the isotherms.

Adsorption of monovalent ions

It turned out that the adsorption isotherms for Na, K and NH_4 were valid for a wide range of total cation concentrations, C_T (Tables 2 & 3, Figs. 1 & 2). The adsorbed quantities could be described as entirely dependent on the ratios between Na, K Ca, Mg and NH_4 concentrations. The only effect of C_T was that different ranges of I values were obtained during the experiments.

The concentrations of NH_4 in the "in situ" soil solutions are very low for the mineral soil but somewhat higher in the humus layer (Bringmark 1980). The average I_{NH_4} at 6 cm in the mineral soil is -1.6. Thus, the low range of the isotherms is important in describing the situation in the soil. However, on occasions with intensive mineralization or after fertilizer additions, the high range of I_{NH_4} could be relevant. The NH_4 isotherms were calculated for the whole range covered by the type 1 experiments (Fig 2, Table 3) and for the range $I > 0.4$. The "fertilization" experiments (type 2) were included in high range isotherms which extended the range upwards (Fig 3, Table 3).

The high range isotherms were not as steep as the low range ones. A decreasing slope was perceivable in the uppermost part of the I-interval (Fig 3). One possible explanation is that concentrations are poor estimates of activities in the intensity variable when C_T reaches several mM, as in the "fertilization" experiments. The I-value for monovalent ions should be corrected by adding the term $\log (f_I \cdot f_{II}^{-0.5})$, f_I and f_{II} being activity coefficients for mono- and divalent ions. This term would increase the I values by approximatively 0.01 at C_T 400 $\mu\text{eq.l}^{-1}$ and 0.05 at C_T 10 000 $\mu\text{eq.l}^{-1}$. These corrections would have additional reducing effects on the slope, especially in the uppermost part of the NH_4 -isotherm. However, it can be concluded that the effects of activity coefficients on I are sufficiently small to be neglected even in the strongest solutions considered in this investigation.

When the ion ratio $C_A^2 C_I^{-1} C_{II}^{-0.5}$ becomes sufficiently high, the other adsorbed ions (G_I and G_{II}) can no longer be treated as an unchanging background. As they are diminished the isotherm slope in equation (3) should decrease, which is a plausible explanation for the behaviour of the NH_4 -isotherm.

The fact that results for NH_4 from experiments with steady levels of C_T and continuously changing C_T conformed to the same adsorption isotherms is additional support for disregarding ΔG_T in the isotherms of monovalent ions.

Adsorption of divalent ions

Experiments at steady levels of C_T resulted in adsorption isotherms for divalent ions that were different for different C_T (Figs. 4 & 5). A given ion ratio in the soil solution (I) corresponded to a larger adsorbed amount at increased C_T . The slope of the adsorption isotherms for divalent ions was increasing with C_T . The isotherms converged in the direction of lowered values of I (Figs. 4 & 5). The divalent ions are probably involved in ion exchange with elements that were not included in the equations that define the adsorption isotherms (Eqs. 2 & 3).

As it has been difficult to find unifying formulations, the adsorption isotherms for a low level of C_T were recorded in the different soil layers (Table 3). These isotherms can be used for approximate predictions of the buffering in situations occurring "in situ", where all ions fluctuate simultaneously as a result of soil processes. If the total concentration is changed, for example because of variations in soil water content, or if C_{Ca} and C_{Mg} are changed relative to a steady background of C_R , other formulations are appropriate. If values are assigned to the denominator $C_I \cdot C_{II}^{0.5}$ in I, the corresponding points on the three isotherms in Figs. 4 & 5 are defined. Such points can be connected to form new isotherms for changing levels of C_T at unchanging C_R . These isotherms will be steeper than those under conditions of steady C_T , i.e. a given increase of the intensity variable (I) will correspond to a larger increase of adsorbed quantity.

Validity of the adsorption isotherms

The adsorption isotherms are empirical relationships. The difficulty to estimate activity coefficients and electrical potentials at the surfaces of the adsorbing solids makes a mechanistic description impossible. As empirical expressions have limited validity, the ranges of I and C_T must be defined, see Table 2.

As a test of validity, the K adsorption isotherm for 0 - 10 cm was applied to the desorption of K in the "NH₄-fertilization" experiments. This meant a transfer from conditions in which C_K and C_R had been altered in opposite directions (experiments 1.1 and 1.2) to conditions in which only C_{NH₄} was changed (experiments 2.1 and 2.2), thus creating a changing C_R in relation to potassium. The range of K intensities obtained in the experiments covered only a small section of the isotherm (Fig. 6). Such applications on small changes are often relevant in simulations of soil processes in nature. The 95% confidence limits for the estimates of ΔK by the isotherm were very wide in relation to the range of ΔK measured in the "fertilization" experiments (Fig. 6). However, the measured data gathered in a more narrow band, probably as a result of a uniform gradient of experimental conditions when only C_{NH₄} was changed. A regression between the ΔK simulated with the adsorption isotherm (ΔK_{sim}) and ΔK measured (ΔK_{msr}) in experiments 2.1 and 2.2 was calculated:

$$\Delta K_{msr} = 0.84 \cdot \Delta K_{sim} - 0.11 \quad r = 0.90 \quad n = 41$$

The slope of this regression does not significantly differ from 1.0 at the 95% level. This means that great changes in the composition of C_R did not have noticeable effects on the isotherm constants in equation 3. The fraction of divalent ions in C_R decreases with increasing C_{NH₄} and the corresponding decrease of I_K, so the formulation of the valency effect was tested by the simulation. Furthermore, the test showed that an isotherm determined on one set of soil samples could be applied to another set.

An analogous test was performed on NH₄+K experiments, type 2.4 (Fig. 6). It resulted in the following regressions

$$\Delta K_{msr} = 5.6 \cdot \Delta K_{sim} + 26 \quad r = 0.82 \quad n = 26$$

for the humus layer and

$$\Delta K_{msr} = 2.6 \cdot \Delta K_{sim} - 0.21 \quad r = 0.92 \quad n = 20$$

for 0-10 cm. Potassium was thus adsorbed to a much greater extent than predicted by the isotherms. The change in the composition of C_R was obviously important in this higher range of K intensities. The valence effect resulting from shifts in the adsorbed amounts of ions of different valence are probably inadequately accounted for in the isotherms as only the composition of the solution is

considered. This demonstrates that caution should be taken in the application of the empirical adsorption isotherms to situations which are very different from the experimental conditions.

Buffer power

The adsorption isotherm for monovalent ions (Eqs.1 & 3) can be written in the form

$$G = \frac{C_A^{2p} 10^q}{C_I^p C_{II}^{0.5p}} \quad (5)$$

Derivation with respect to C_A yields

$$\frac{dG}{dC_A} = \frac{2p \cdot 10^q}{C_I^p C_{II}^{0.5p} C_A^{(1-2p)}} \quad (6)$$

which is the buffer power of the soil, β ($\text{dm}^3_w \cdot \text{g}^{-1}$). For divalent ions the expression is

$$\frac{dG}{dC_A} = \frac{p \cdot 10^q}{C_I^p C_{II}^{0.5p} C_A^{(1-p)}} \quad (7)$$

A precondition for the derivations is that C_I and C_{II} are independent of C_A . In reality they may interact through the ion exchange. For use in models it is convenient to have averages over intervals of C_A , here exemplified for a monovalent ion:

$$b = \frac{2p \cdot 10^q}{C_I^p C_{II}^{0.5p}} \cdot \frac{1}{C_1 - C_2} \cdot \int_{C_2}^{C_1} C_A^{(2p-1)} dC_A$$

$$b = \frac{10^q}{C_I^p C_{II}^{0.5p}} \cdot \frac{C_1^{2p} - C_2^{2p}}{C_1 - C_2}$$

where b is the estimate of β and C_1 and C_2 are the boundary concentrations. The average for divalent ions is calculated in a corresponding way. The average composition of the solution from lysimeter investigation in the same soil as that of the adsorption studies has been reported earlier (Bringmark 1980). The solution entering the humus layer had the following mean concentrations in the first half of the growing season: NH_4 90, Na 20, K 75, Ca 60 and Mg 20, all in μM . At 6 cm in the mineral soil the average composition of the solution was NH_4 7, Na 180, K 50, Ca 50 and Mg 50 μM . These concentrations have been used for estimating the buffer power in the interval $0 < C_A < 200 \mu\text{M}$. The values have been expressed on a volume basis in order to permit comparisons between soil layers using the specific weights in Table 1.

The following buffer powers (b) were found in the humus layer:

NH_4 3.8, Na 1.3, K 1.7, Ca 12.1 and Mg 6.7 ($\text{dm}_w^3 \cdot \text{dm}_s^{-3}$)

The indices stand for water and soil respectively. The figures for the mineral soil layers were NH_4 2.0, Na 0.9, K 4.3, Ca 1.6 and Mg 0.69 at 0 - 10 cm and NH_4 1.7, K 2.6, Ca 0.30 and Mg 0.47 in the 10 - 20 cm layer. It is obvious that there is a large adsorption of divalent ions relative to monovalent in the humus layer. In the mineral soil the relative importance of the divalent ions decreases with depth. This is probably coupled to the gradient of organic content (Table 1).

After transferring the volumetric buffer powers to an areal basis, the buffer capacities ($\text{dm}_w^3 \cdot \text{m}_s^{-2}$) of the soil layers can be compared. The factor for this conversion was 30 for the humus layer and 100 for the mineral soil. The comparison showed that the 10 cm layers of the mineral soil had a larger capacity for the adsorption of monovalent ions, and less capacity for divalent ions than the humus layer.

Influence on uptake and leaching

The buffer power affects leaching and uptake in roots by lowering the transport rates. Using the average buffer power (b), the rate of leaching (L) can be expressed as

$$L = k_L \cdot N \quad (\mu\text{mole} \cdot \text{dm}^{-3} \text{ day}^{-1}) \quad (8)$$

$$k_L = \frac{v}{z \cdot b} \quad b = \frac{N}{C_A}$$

where k_L is a rate coefficient (day^{-1}), v is water flow in the vertical direction ($\text{dm}_w^3 \text{ dm}_s^{-2} \text{ day}^{-1}$), z is soil depth (dm) and N is the total adsorbed plus dissolved quantities of an ion ($\mu\text{mole dm}_s^{-3}$). N is approximately equal to the adsorbed amount (G).

Baldwin (1975) has given an approximative expression for the rate of diffusion to roots. This is:

$$U = k_U \cdot N \quad (\mu\text{mole dm}^{-3} \text{ day}^{-1}) \quad (9)$$

$$k_U = \frac{R}{b}$$

where k_U is a rate coefficient (day^{-1}) and R ($\text{dm}_w^3 \text{ dm}_s^{-3} \text{ day}^{-1}$), a factor accounting for the influence of root and pore geometries and diffusion constants (Bosatta 1980). The expression can not be applied to Na as this element is selectively excluded by the roots.

The condition of steady input

The size of an ion pool (N) is controlled by the rates of leaching and uptake and the rate of input from internal and external sources (S).

$$\frac{dN}{dt} = S - k \cdot N \quad k = k_U + k_L = \frac{R + \dot{v}/z}{b}$$

The solution to this equation, if k and S are assumed constant, is:

$$N(t) = \frac{S}{\bar{k}} + (N_0 - \frac{S}{\bar{k}}) e^{-kt} \quad (10)$$

where N_0 is the starting value at $t=0$. Steady state (N_S) is reached when $dN/dt=0$, i.e.,

$$N_S = \frac{S}{\bar{k}} \quad (11)$$

The rate of change as well as the size of N at each time depends on the buffer power. Analytical solutions according to equation (10) require that b is independent of N , which is the case when the average estimate of β is used.

The quantity absorbed by roots during periods of steady input rates (S) is:

$$U_{0-t} = k_u \int_0^t N(t') dt' = \frac{k_u}{k} \left(St + \left(N_0 - \frac{S}{k} \right) (1 - e^{-kt}) \right) \quad (12)$$

The quantity leached is:

$$L_{0-t} = k_L \int_0^t N(t') dt = \frac{k_L}{k} \left(S \cdot t + \left(N_0 - \frac{S}{k} \right) (1 - e^{-kt}) \right) \quad (13)$$

By dividing uptake with leaching the following ratio is generated

$$\frac{U_{0-t}}{L_{0-t}} = \frac{k_u}{k_L} = \frac{R}{v/z}$$

So the fraction taken by roots is independent of the buffer power when the input is constant in time.

Comparison with lysimeters

The value of R was calculated according to the expression of Baldwin (1975) using the following rough values on the required parameters: water content $0.1 \text{ dm}_w^3 \text{ dm}_s^{-3}$, diffusion constant $0.01 \text{ dm}_w^2 \text{ day}^{-1}$, root diameter 0.005 dm and root length 5 dm dm_s^{-3} in the humus layer and 0.8 at $0 - 10 \text{ cm}$. The root parameters include pine, heather and cowberry (H Persson pers. comm.). The estimate of R from the described parameters was $0.4 \text{ dm}_w^3 \text{ dm}_s^{-3} \text{ day}^{-1}$ for the humus layer and 0.03 for $0 - 10 \text{ cm}$.

Using these estimates of R , the rate coefficient $k_u \text{ day}^{-1}$ becomes $0.4/b$ for the humus layer and $0.03/b$ for the mineral soil layer $0 - 10 \text{ cm}$. The average water flow (v) is roughly $0.015 \text{ dm}_w^3 \text{ dm}_s^{-2} \text{ day}^{-1}$. The thickness (z) of 0.3 dm for the humus layer and 1 dm in the mineral soil results in k_L values of $0.05/b$ and $0.015/b$ for the respective layer. The ratios between uptake and leaching, being

equal to k_U/k_L were then 8 for the humus layer and 2 for the mineral soil. A very effective interception in the humus layer has actually been observed for NH_4 in lysimeters (Bringmark 1980). However, a larger fraction of K, Ca and Mg are leached in the lysimeters than would be expected from k_U/k_L . At an internal ranking of the fraction taken up of the three ions Ca is placed first in the humus layer and K in the mineral soil. This is correlated with Ca having the greatest buffer power in the humus layer and K in the mineral soil, so an influence of the buffer power on the uptake/leaching ratio is probable.

Variable soil conditions

Two of the parameters controlling the uptake/leaching ratio are highly variable over time i.e., root length (Persson 1980) and water flow. Water flow appears as short flushes in the sandy soil. K, Ca and Mg are transported from the litter layer to the humus layer and the mineral soil with the percolating solution, the input being almost proportional to the water flow. In contrast, the input of NH_4 from the litter layer as well from internal sources in the humus layer is less dependent on water flow (Bringmark 1980). This different character of the input is of great importance for the uptake efficiency, as the rate coefficient for leaching (k_L) is greatly increased during flow events.

Applications of equations (10), (11), (12) and (13) on the following theoretical example illustrates the influence of b on the transports of K, Ca and Mg. The example deals with the humus layer during two weeks, when the water flow is set to $0.10 \text{ dm}_w^3 \text{ dm}_s^{-2} \text{ day}^{-1}$ in the first week and zero the second. Corresponding values for k_L are $0.33/b$ and 0 . k_U is $0.4/b$. The starting values (N_0), assumed to have been lowered by uptake, are set to 75% of the steady state values for the flow period ($N_S = S/k$). The values of N_0 and N_S are different for the three ions, K, Ca and Mg, depending on the input and their respective values of b , which are 1.7, 12.1 and $6.7 \text{ dm}_w^3 \text{ dm}_s^{-3}$.

During the week with water flow, the input (S) of K, Ca and Mg can be expressed as the concentrations times water flow in the inflowing solution. These concentrations are 75, 60 and 20 μM for K, Ca and Mg respectively. After the first seven days $N(t)$ increased to 99, 83 and 88% of N_S for the three ions respectively.

This means that steady state was reached fastest for K, because its steady state quantity was smallest in relation to the rate of input. K had also the highest rates of leaching and uptake in relation to the input during the first week.

$N(t)$ obtained after seven days (N_7), expressed as percentage of the input quantity ($S.t$), was 33% for K, 199% for Ca and 116% for Mg, figures that are almost proportional to the respective b value. N_7 was the start value for the remaining seven days of no water flow. There was no input and no leaching during this second period, so the uptake (U_{7-14}) was calculated with

$$U_{7-14} = N_7 (1 - e^{-k_u \cdot 7}) \quad (14)$$

Even if a lowered rate coefficient (k_u) at increasing b counteracted the favourable effect of an increased N_7 , the result was an increasing uptake when b rose in the relevant range. The uptake/leaching ratios for the whole simulation of the two-week period were 1.9 for K, 2.4 for Ca and 2.3 for Mg, i.e. the buffer power has an influence under conditions of variable input. Variations in the root geometry would also bring out effects of the buffer-power on the uptake/leaching ratio.

Summary of conclusions

1. Adsorption isotherms according to equations (1), (2) and (3) are valid for monovalent ions in the lower range of their I -values, irrespective of the level of C_T or the composition of C_R . This is the range which is most relevant for conditions "in situ".
2. The effect of variable exchange capacity at different levels of C_T must be considered for the isotherms of divalent ions. The variable capacity is probably caused by exchange with ions which are not included in equations (1), (2) and (3).
3. The adsorption isotherms according to equations (1), (2) and (3) have limited validity in the high range of I -values. Special caution should be taken in applications to conditions in which the composition of C_R is differing from those of the original isotherm determination.

4. In situations of constant input, the uptake/leaching ratio in the soil-root system is independent of the buffer power resulting from adsorption.
5. The buffer power is important for the uptake/leaching ratio over longer periods if input and leaching occur simultaneously during short water flow events within these periods.

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TABLE 1 Some properties of the investigated forest podsol

	humus layer	mineral soil 0-10 cm	mineral soil 10-20 cm
Spec. weight (kg. dm ⁻³)	0.066 ^x	1.09	1.21
Fine material diam. < 0.06 mm (% d.w)		11.2	7.5
Carbon (% d.w.)	31	1.79	0.62
Extractable in 1M NH ₄ Cl (umole. g ⁻¹)			
Na	1.8	0.16	0.13
K	10	0.59	0.22
Ca	23	0.35	0.09
Mg	5.5	0.12	0.06
Al	15	7.3	0.8
H	32	0.42	0.01
pH of 1M NH ₄ Cl extracts	3.0	4.4	4.7

x) based on an estimated layer thickness of 3 cm

TABLE 2 Experimental conditions at the determinations of adsorption isotherms.

nr	ion	type of experiment	range of I-values	range of C_T ($\mu\text{eq.l}^{-1}$)
humus layer				
1	NH_4	1.1	$-2.4 < I < 2.2$	710 - 1.860
2	NH_4	1.1 2.2	$0.4 < I < 2.2$	710 - 9.800
3	Na	1.1	$-0.1 < I < 2.7$	820 - 2.300
4	K	1.1	$1.2 < I < 3.6$	990 - 2.700
5	Ca	1.1	$-1.6 < I < -1.1$	~ 500
6	Mg	1.1	$-2.2 < I < -1.4$	~ 520
mineral soil, 0 - 10 cm				
11	NH_4	1.2	$-0.8 < I < 2.8$	340 - 1.460
12	NH_4	1.2 2.1 2.3	$0.4 < I < 3.7$	380 - 4.800
13	Na	1.1	$0.3 < I < 4.2$	240 - 2.100
14	K	1.1 1.2	$-1.8 < I < 4.0$	380 - 2.200
15	Ca	1.1	$-1.7 < I < 0.2$	~ 490
16	Mg	1.1	$-2.1 < I < -0.1$	~ 470
mineral soil, 10 - 20 cm				
21	NH_4	1.1	$-1.6 < I < 2.3$	~ 1.200
22	K	1.1	$-2.1 < I < 4.1$	690 - 2.000
23	Ca	1.1	$-1.6 < I < 0.3$	~ 390
24	Mg	1.1	$-2.2 < I < 0.2$	~ 420

TABLE 3 Adsorption isotherms for different ions and soil layers.
 Adsorbed amounts ($\Delta G + G_{ex}$) in $\mu\text{mole.g}^{-1}$, intensity variable
 (I) defined in the text.

nr	adsorption isotherm	corr. coeff.	number of equilibrations
humus layer			
1	$\log (\Delta\text{NH}_4 + 0.3) = 0.42 \cdot I + 0.36$	0.95	54
2	$\log (\Delta\text{NH}_4 + 0.3) = 0.34 \cdot I + 0.44$ ^x	0.89	58
3	$\log (\Delta\text{Na} + 1.8) = 0.51 \cdot I - 0.14$	0.95	25
4	$\log (\Delta\text{K} + 10) = 0.36 \cdot I + 0.14$	0.90	28
5	$\log (\Delta\text{Ca} + 23) = 0.22 \cdot I + 1.7$	0.92	28
6	$\log (\Delta\text{Mg} + 5.5) = 0.46 \cdot I + 1.7$	0.93	28
mineral soil, 0 - 10 cm			
11	$\log (\Delta\text{NH}_4 + 0.16) = 0.45 \cdot I - 0.98$	0.96	54
12	$\log (\Delta\text{NH}_4 + 0.16) = 0.31 \cdot I - 0.71$ ^x	0.93	71
13	$\log (\Delta\text{Na} + 0.16) = 0.28 \cdot I - 1.29$	0.90	27
14	$\log (\Delta\text{K} + 0.60) = 0.105 \cdot I - 0.24$	0.88	96
15	$\log (\Delta\text{Ca} + 0.35) = 0.16 \cdot I - 0.39$	0.94	25
16	$\log (\Delta\text{Mg} + 0.12) = 0.32 \cdot I - 0.60$	0.96	27
mineral soil, 10 - 20 cm			
21	$\log (\Delta\text{NH}_4) = 0.35 \cdot I - 0.99$	0.97	36
22	$\log (\Delta\text{K} + 0.22) = 0.16 \cdot I - 0.58$	0.95	48
23	$\log (\Delta\text{Ca} + 0.09) = 0.65 \cdot I - 0.71$	0.85	20
24	$\log (\Delta\text{Mg} + 0.06) = 0.44 \cdot I - 0.70$	0.88	28

x) $I > 0.4$

Legends to figures:

- Fig. 1 K adsorption isotherms for 0-10 cm in the mineral soil. 95% confidence limits on the prediction of the quantity variable (Q) from the regression are shown.
- Fig. 2 NH_4 adsorption isotherm, 0-10 cm, for the lower range of I-values. 95% confidence limits on the prediction of Q are shown.
- Fig. 3 NH_4 adsorption isotherm, 0-10 cm, for the higher range of I-values. 95% confidence limits on the prediction of Q are shown.
- Fig. 4 Ca adsorption isotherm for different levels of C_T , 0-10 cm.
- Fig. 5 Mg adsorption isotherms for different levels of C_T , 0-10 cm.
- Fig. 6 Validation of the K adsorption isotherm in Fig. 1 with data from "fertilization" experiments. 95% confidence limits on the prediction of ΔK are shown.

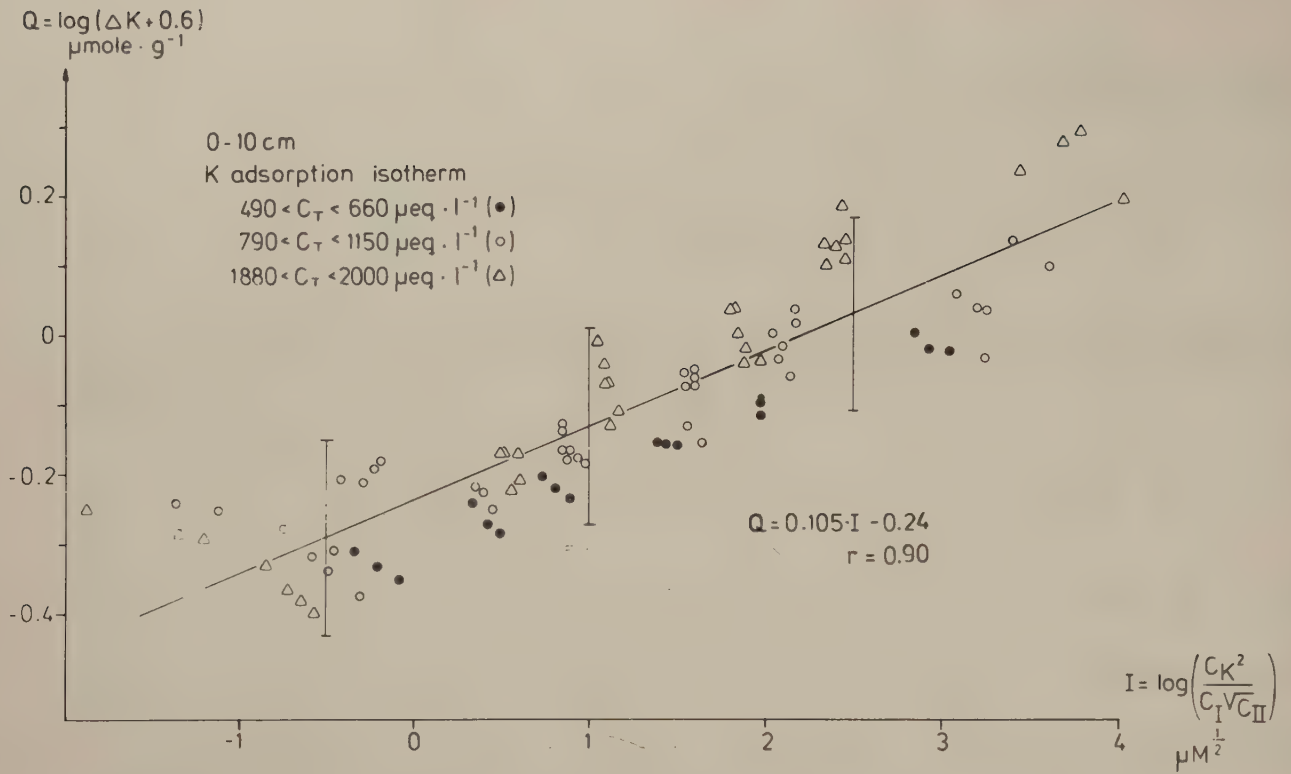


Fig. 1

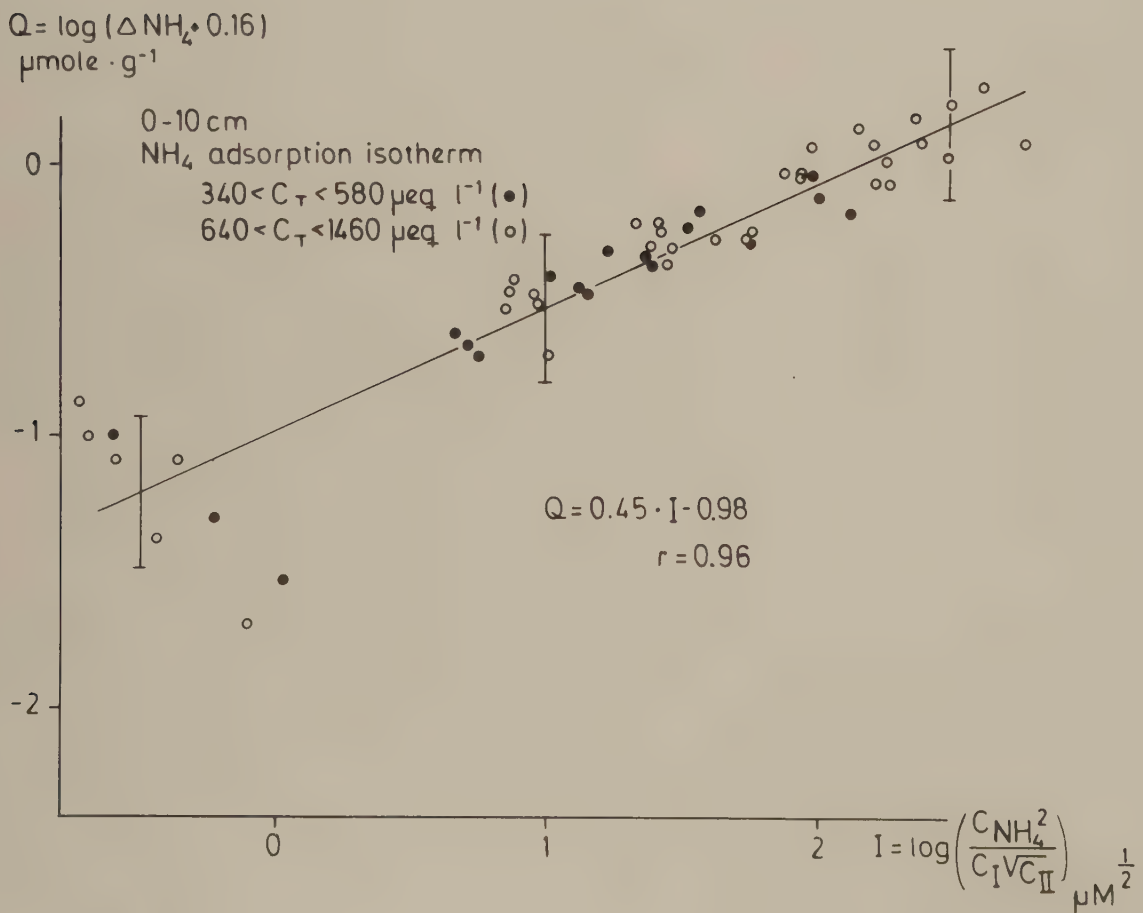


Fig. 2

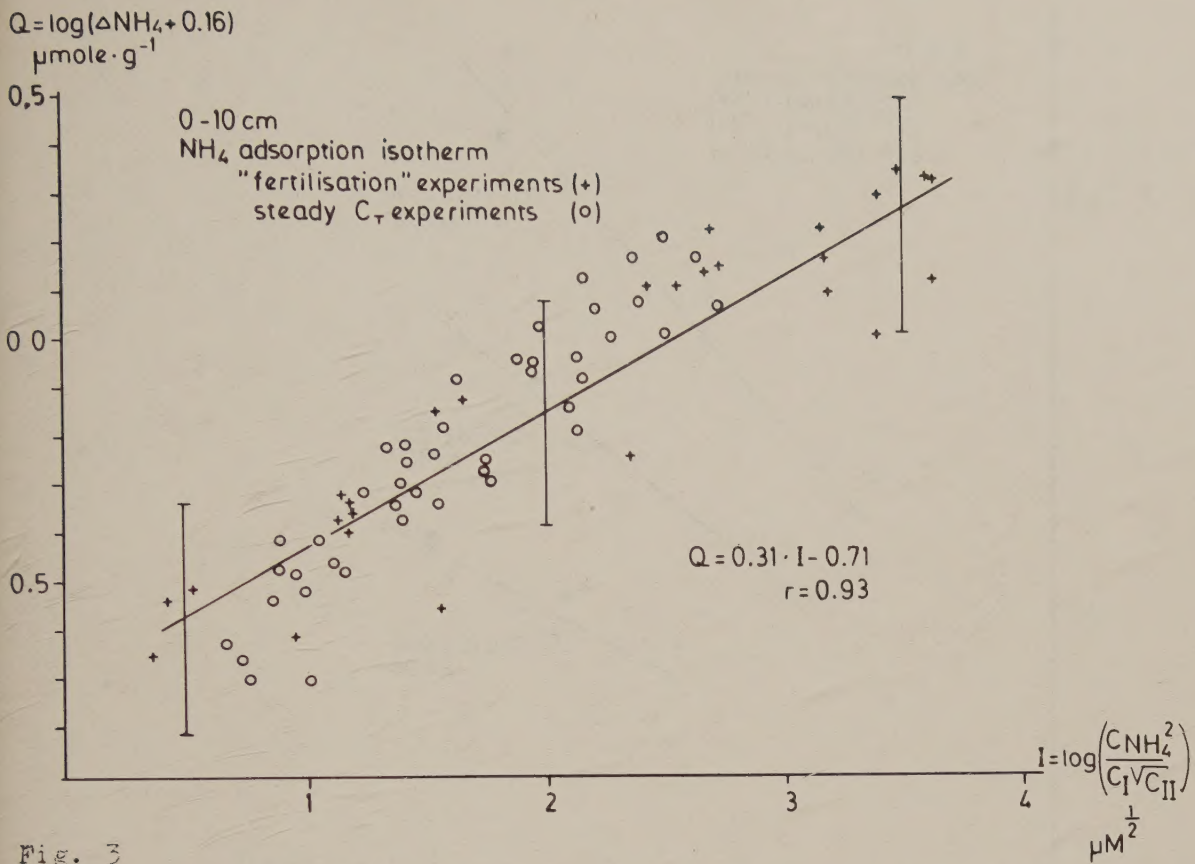


Fig. 3

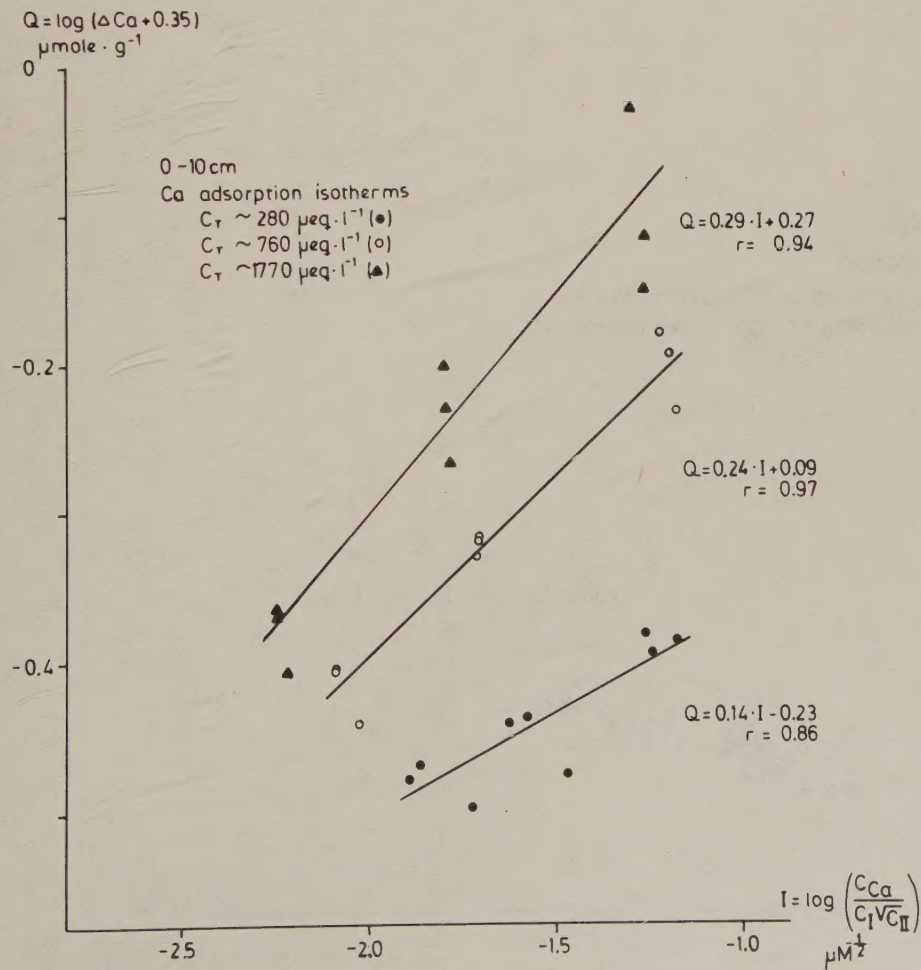


Fig. 4

$$Q = \log(\Delta \text{Mg} + 0.12)$$

$$\mu\text{mole} \cdot \text{g}^{-1}$$

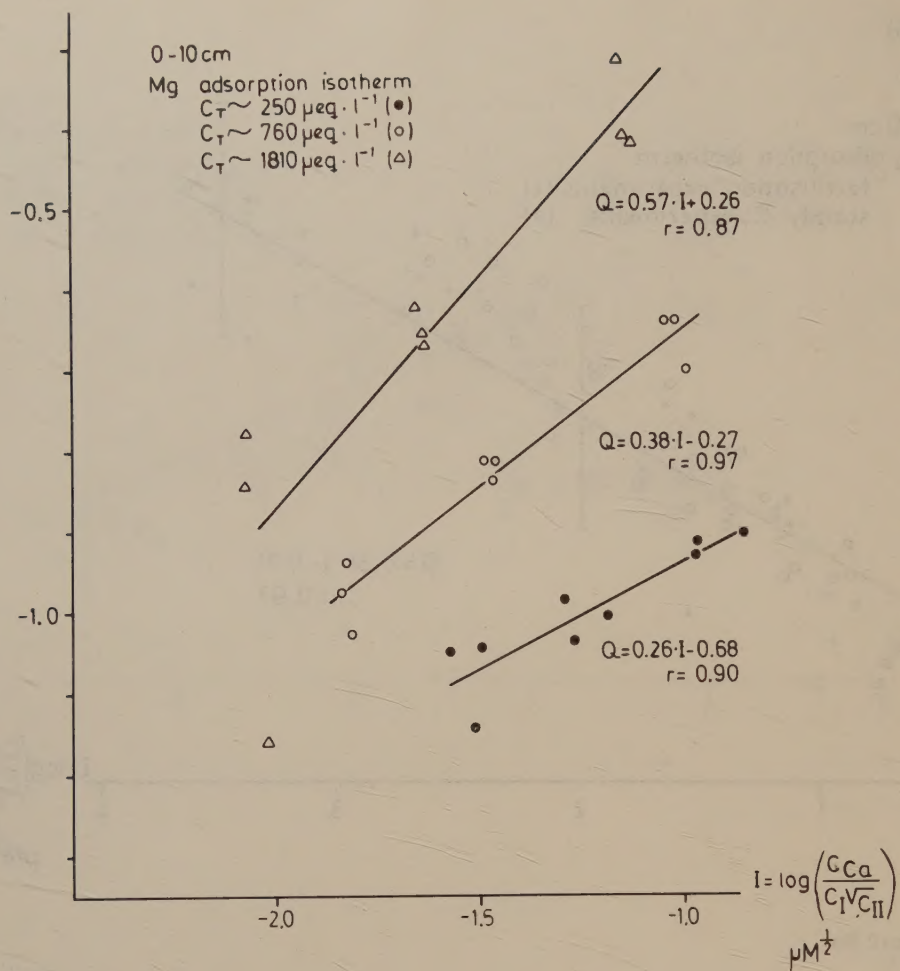


Fig. 5

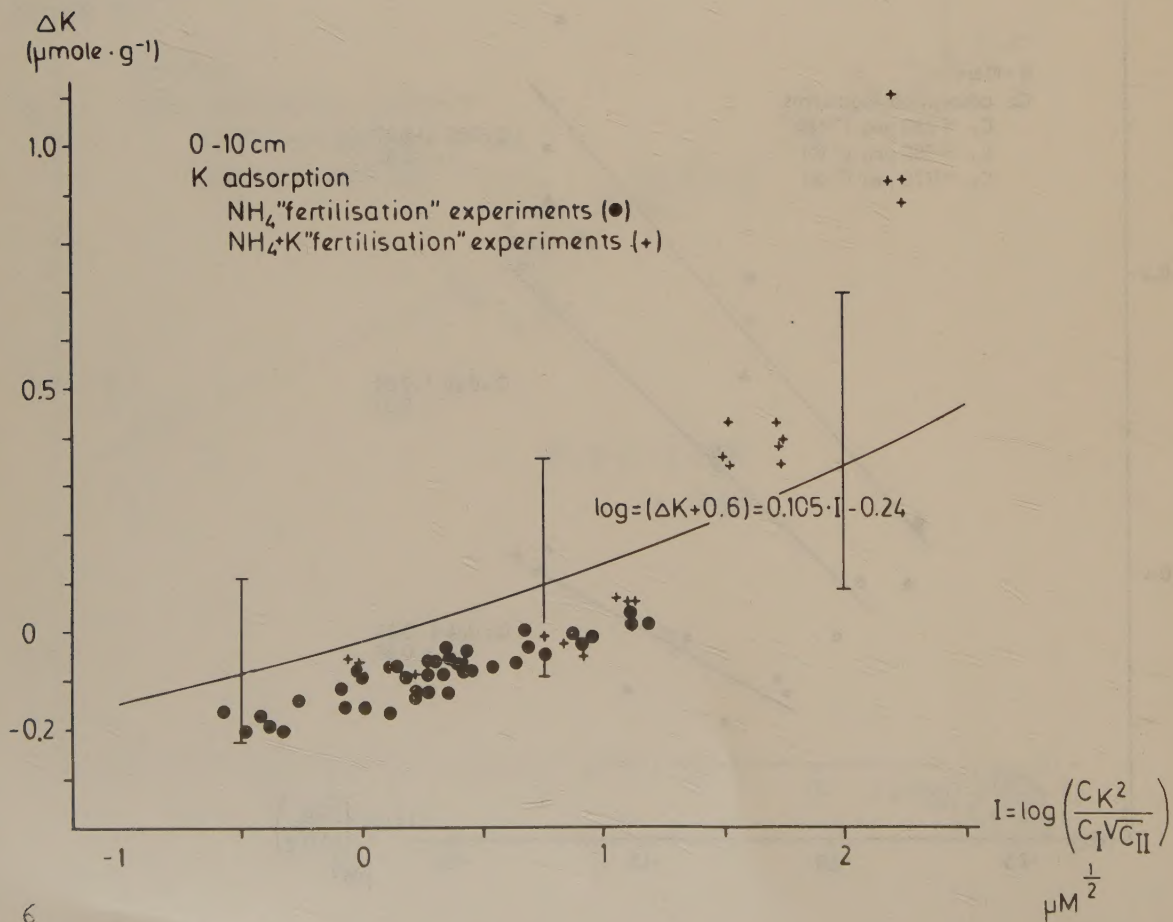


Fig. 6

